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(54) Title: COMPOSITE SOLID POLYMER ELECTROLYTE MEMBRANES

(57) Abstract

The present invention relates to composite solid polymer electrolyte membranes (SPEMs) which include a porous polymer substrate interpenetrated with an ion-conducting material. The SPEMs are useful in electrochemical applications, including fuel cells and electrodialysis.

What is claimed is:

1. A composite solid polymer electrolyte membrane (SPEM) comprising a porous polymer substrate interpenetrated with an ion-conducting material, wherein the SPEM is substantially thermally stable to temperatures of at least about 100°C.

2. The SPEM of claim 1, wherein the SPEM is stable from at least about 100°C to at least about 175°C.

3. The SPEM of claim 1, wherein the SPEM is stable from at least about 100°C to at least about 150°C.

4. The SPEM of claim 1, wherein the SPEM is stable from at least about 120°C to at least about 175°C.

5. The SPEM of claim 1 wherein

(i) the porous polymer substrate comprises a homopolymer or copolymer of a liquid crystalline polymer or a solvent soluble thermoset or thermoplastic aromatic polymer, and

(ii) the ion-conducting material comprises a homopolymer or copolymer of at least one of a sulfonated, phosphonated or carboxylated ion-conducting aromatic polymer or a perfluorinated ionomer.

6. A composite solid polymer electrolyte membrane (SPEM) comprising a porous polymer substrate interpenetrated with an ion-conducting material, wherein

(i) the porous polymer substrate comprises a homopolymer or copolymer of a liquid crystalline polymer or a solvent soluble thermoset or thermoplastic aromatic polymer, and

(ii) the ion-conducting material comprises a homopolymer or copolymer of at least one of a sulfonated, phosphonated or carboxylated ion-conducting aromatic polymer or a perfluorinated ionomer.

7. The SPEM of claims 1 or 6, wherein the porous substrate polymer comprises a microinfrastructure substantially interpenetrated with the ion-conducting material.

8. The SPEM of claims 1 or 6, wherein the porous polymer substrate comprises an extruded or cast film.

9. The SPEM of claim 5, wherein the SPEM substantially stable to temperatures of at least about 100°C.

10. The SPEM of claims 5 or 6, wherein the liquid crystalline substrate polymer comprises a lyotropic liquid crystalline polymer.

11. The SPEM of claim 10, wherein the lyotropic liquid crystalline substrate polymer comprises at least one of a polybenzazole (PBZ) and polyaramid (PAR) polymer.

12. The SPEM of claim 11, wherein the polybenzazole substrate polymer comprises a homopolymer or copolymer of at least one of a polybenzoxazole (PBO), polybenzothiazole (PBT) and polybenzimidazole (PBI) polymer and the polyaramid polymer comprises a homopolymer or copolymer of a polypara-phenylene terephthalamide (PPTA) polymer.

13. The SPEM of claims 5 or 6, wherein the thermoset or thermoplastic aromatic substrate polymer comprises at least one of a polysulfone (PSU), polyimide (PI), polyphenylene oxide (PPO), polyphenylene sulfoxide (PPSO), polyphenylene sulfide (PPS), polyphenylene sulfide sulfone ($PPS/SO_2$), polyparaphenylene (PPP), polyphenylquinoxaline (PPQ), polyarylketone (PK) and polyetherketone (PEK) polymer.

14. The SPEM of claim 13, wherein the polysulfone substrate polymer comprises at least one of a polyethersulfone (PES), polyetherethersulfone (PEES), polyarylethersulfone (PAS), polyphenylsufone (PPSU) and polyphenylenesulfone ($PPSO_2$) polymer; the polyimide (PI) polymer comprises a polyetherimide (PEI) polymer; the polyetherketone (PEK) polymer comprises at least one of a polyetheretherketone (PEEK),

polyetherketone-ketone (PEKK), polyetheretherketone-ketone (PEEKK) and polyetherketoneetherketone-ketone (PEKEKK) polymer; and the polyphenylene oxide (PPO) polymer comprises a 2,6-diphenyl PPO polymer.

15. The SPEM of claims 1 or 6, wherein the pore size of the porous substrate polymer is from about 10 Å to about 2000 Å.

16. The SPEM of claim 15, wherein the pore size is from about 500 Å to about 1500 Å.

17. The SPEM of claim 15, wherein the pore size is from about 500 Å to about 1000 Å.

18. The SPEM of claims 1 or 6, wherein the ion-conducting material has an ion-conductivity from about 0.01 S/cm to about 0.50 S/cm.

19. The SPEM of claim 18, wherein the ion-conducting material has an ion-conductivity greater than about 0.1 S/cm.

20. The SPEM of claims 5 or 6, wherein the ion-conducting aromatic polymer comprises wholly aromatic ion-conducting polymer.

21. The SPEM of claims 5 or 6, wherein the ion-conducting aromatic polymer comprises a sulfonated, phosphonated or carboxylated polyimide polymer.

22. The SPEM of claim 21, wherein the polyimide polymer is fluorinated.

23. The SPEM of claim 20, wherein the sulfonated wholly-aromatic ion-conducting polymer comprises a sulfonated derivative of at least one of a polysulfone (PSU), polyphenylene oxide (PPO), polyphenylene sulfoxide (PPSO), polyphenylene sulfide (PPS), polyphenylene sulfide sulfone (PPS/$SO_2$), polyparaphenylene (PPP), polyphenylquinoxaline (PPQ), polyarylketone (PK), polyetherketone (PEK), polybenzazole (PBZ) and polyaramid (PAR) polymer.

24. The SPEM of claim 23, wherein

(i) the polysulfone polymer comprises at least one of a polyethersulfone (PES), polyetherethersulfone (PEES), polyarylsulfone, polyarylethersulfone (PAS), polyphenylsulfone (PPSU) and polyphenylenesulfone ($PPSO_2$) polymer,

(ii) the polybenzazole (PBZ) polymer comprises a polybenzoxaxole (PBO) polymer;

(iii) the polyetherketone (PEK) polymer comprises at least one of a polyetheretherketone (PEEK), polyetherketone-ketone (PEKK), polyetheretherketone-ketone (PEEKK) and polyetherketoneetherketone-ketone (PEKEKK) polymer; and

(iv) the polyphenylene oxide (PPO) polymer comprises a 2,6-diphenyl PPO polymer.

25. The SPEM of claims 5 or 6, wherein the perfluorinated ionomer comprises a homopolymer or copolymer of a perfluorinated vinyl ether.

26. The SPEM of claim 25, wherein the perfluorinated vinyl ether is carboxyl- (COOH), phosphonyl- ($PO(OH)_2$) or sulfonyl- ($SO_3H$) substituted.

27. The SPEM of claim 1, wherein the ion-conducting material comprises at least one of a polystyrene sulfonic acid (PSSA), poly(trifluorostyrene) sulfonic acid, trifluorostyrene, polyvinyl phosphonic acid (PVPA), polyvinyl carboxylic acid (PVCA) and polyvinyl sulfonic acid (PVSA) polymer.

28. The SPEM of claims 1 or 6, wherein the porous polymer substrate comprises a homopolymer or copolymer of at least one of a substituted or unsubstituted polybenzazole polymer, and wherein the ion-conducting material comprises a sulfonated derivative of a homopolymer or copolymer of at least one of a polysulfone (PSU), polyphenylene sulfoxide (PPSO) and polyphenylene sulfide sulfone ($PPS/SO_2$) polymer.

29. The SPEM of claim 28, wherein the polysulfone polymer comprises at least one of a polyethersulfone (PES) and polyphenylsulfone (PPSU) polymer.

30. The SPEM of claims 1 or 6, wherein the SPEM has a specific resistance from about 0.2 to about 20 $\Omega$*$cm^2$.

31. The SPEM of claims 1 or 6, wherein the SPEM has a specific resistance of less than about 0.2 $\Omega$*$cm^2$.

32. The SPEM of claims 1 or 6, wherein the SPEM has a thickness from about 0.1 mil. to about 2.0 mil.

33. The SPEM of claim 32, wherein the thickness is less than about 0.5 mil.

34. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing a mixture of a substrate polymer and an ion-conducting material in a common solvent and casting or extruding a composite membrane from the mixture.

35. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing a mixture of the substrate polymer and the ion-conducting material and extruding or casting a composite film directly from the mixture.

36. A method of producing a composite solid polymer electrolyte membrane (SPEM) comprising the steps of performing a sulfonation reaction within the pores of a polymer substrate, wherein the SPEM is substantially thermally stable to temperatures of at least about 100°C.

37. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of solubilizing the ion-conducting polymer and imbibing the porous polymer substrate with the ion-conducting polymer.

38. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing the polymer substrate and subsequently impregnating the substrate with appropriate monomers which are then polymerized in-situ to form the SPEM.

39. A device comprising a composite solid polymer electrolyte membrane in accordance with claims 1 or 6.

40. The device of claim 39, wherein the device is a fuel cell.

41. The device of claim 40, wherein the fuel cell is a direct methanol fuel cell or a hydrogen/air fuel cell.

42. A method of decreasing methanol crossover rate in the fuel cell of claim 44 by using the SPEM of claim 1 in an electrochemical reaction in the fuel cell.

43. The device of claim 40, wherein the fuel cell is used to supply power to an electronic device.

44. The device of claim 39, wherein the device is a system for membrane-based water electrolysis or chloralkali electrolysis.

45. The device of claim 39, wherein the device is a dialysis, electrodialysis or electrolysis system.

46. The device of claim 39, wherein the device is a pervaporation or gas separation. system.

47. The device of claim 39, wherein the device is a water splitting system for recovering acids and bases from waste water solutions.

48. The device of claim 39, wherein the device is an electrode separator in a battery.

49. The device of claim 41, wherein the methanol permeation rate in the direct methanol fuel cell is less than about 0.01 $cm^3/sec$.

# The Gas Permeability and Ionic Conductivity Properties of the Microcomposite Membrane will be Adjusted by Controlling the Concentration of Infiltrated Ion-Conducting Polymer and its Degree of Sulfonation

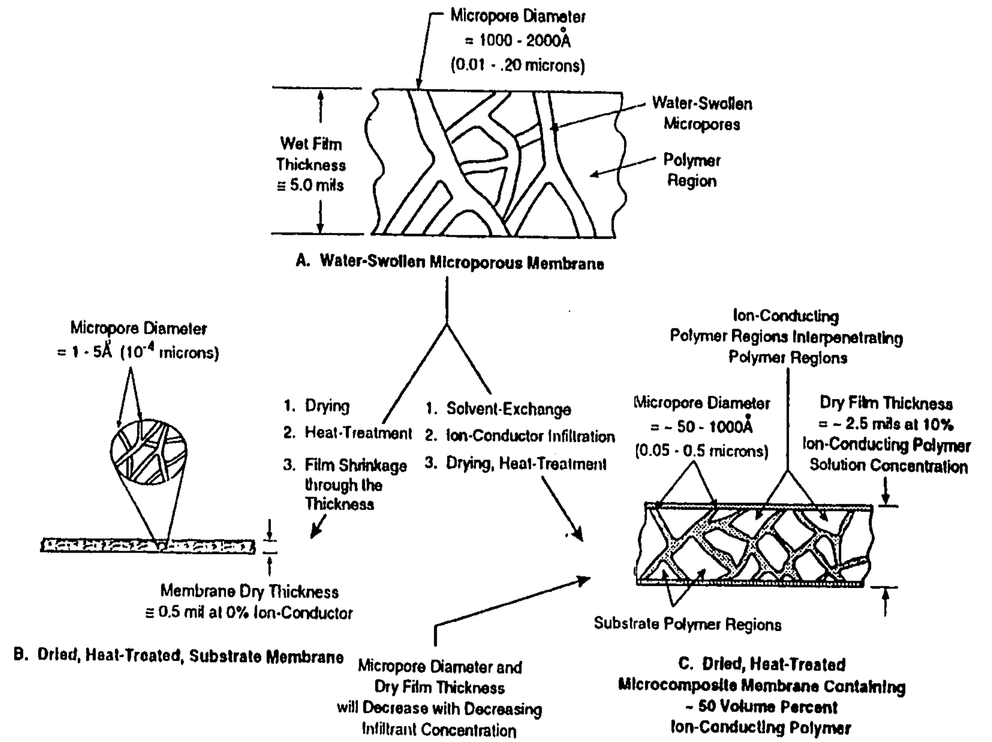
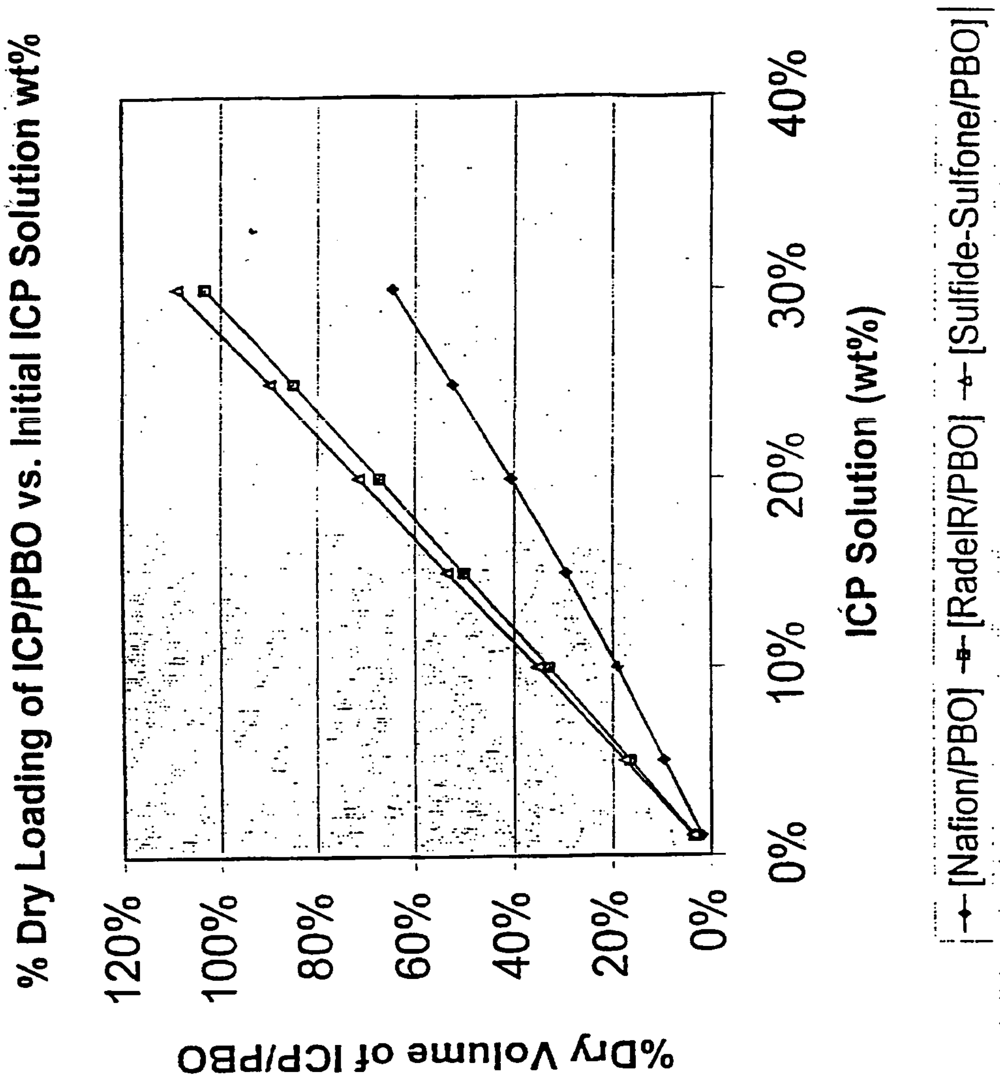



Fig 1


% Dry Loading of ICP/PBO vs. Initial ICP Solution wt%
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120%
100%
80%
60%
40%
20%
0%
0%
10%
20%
30%
40%
ICP Solution (wt%)
[Nafion/PBO]
[RadelR/PBO]
[Sulfide-Sulfone/PBO]

Fig 2